Gas Chromatography/Fourier Transform Infrared Spectrometry Analysis of Semivolatile Coal Gasification Pollutants

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Gas chromatography/Fourier transform infrared spectrometry has been used to analyze a sample of semivolatile organic pollutants collected during a coal gasification using a bench scale coal gasifier. The compounds identified include benzene, phenol, naphthalene, and some of their alkyl derivatives.

Index Headings: GC/FT-IR; Coal gasification.

INTRODUCTION

The decreased supply of petroleum during the past decade has led to a search for alternate energy sources. One such source, coal, is readily available in the United States and represents one of the most promising alternatives. Gasification is currently being investigated and commercialized as a possible mechanism for converting the energy in coal into a usable form.

The potential pollution problems associated with coal gasification are being studied at the Research Triangle Institute using a fixed bed laboratory scale gasifier. The major goal of the project is the assessment and analysis of inorganic and organic pollutants associated with the coal gasification process. To this end, three major fractions are collected and analyzed: volatiles (glass bulb collection), semivolatile organics (XAD-2 resin sorbent), and nonvolatile organics (tar/condensate). Details of this program have been described elsewhere.[1] The analysis of semivolatile compounds is best accomplished by gas chromatographic separation followed by on-line detection. The detector most often used is the mass spectrometer.[2-10] The complexity of the samples and the need for comprehensive identification of the components requires a spectrometric detector, since retention time alone does not provide sufficient information. While mass spectrometry is the most widely used spectrometric gas chromatography (GC) detector, Fourier transform infrared spectrometry (FT-IR) can also provide compound identifications and, in fact, is generally more able to distinguish among isomers.

The purpose of this paper is to illustrate the utility of GC/FT-IR for the analysis of coal gasification pollutants.

I. EXPERIMENTAL

A. Coal Gasification and Sampling Parameters. The sample was taken from the process stream of a semibatch bench scale coal gasifier which has been described previously.[1] The charge for this gasification run was 1250 g of Western Kentucky no. 9 (8 by 16 mesh). The sample shown is from the first 14 min after the coal charge was dropped into the gasifier and represents the pyrolysis phase of the run (surge) before steady state temperatures were attained. The upper gasifier temperatures varied from 725 to 922°C over this period. Pressure was maintained at 1400 kPa (200 psi). The volume of sample collected was 652 liters (STP).

The gasifier effluent stream passed through a condensate trap, a glass fiber filter, and a 150 g XAD-2 (Rohm & Haas) resin bed (5 cm i.d. by 25 cm).

B. Sampling Extraction and Workup. The XAD-2 resin from the trap was placed into a tared jar, weighed, and thoroughly mixed. A 20 g aliquot of the XAD-2 was placed in a pre-extracted cellulose thimble and extracted with methylene chloride for 20 h in a Soxhlet extractor. The extract (~150 ml) was evaporated to ~5 ml in a Kuderna-Danish evaporator and the volume was further reduced to 1 ml using a micro-Kuderna-Danish receiver. This sample was then submitted for GC/FT-IR analysis.

C. GC/FT-IR Analysis. The sample was analyzed using a Nicolet 7199 FT-IR with the Nicolet GC-7000 GC/FT-IR accessory. The sample (1 μl, highly concentrated) was chromatographed using a Varian 3700 GC equipped with a thermal conductivity (TC) detector. Chromatography conditions were as follows: 2 mm i.d. by 180 cm glass column packed with 3% OV-17 on Chromosorb G(AW) 100/120 mesh; carrier gas, 30 ml/min of helium; injector temperature, 222°C; TC detector temperature, 283°C; column temperature, 50°C for 3 min, programmed at 8°/min to 240°, then held for 10 min. The GC column effluent was transferred from the TC detector to a 3 mm i.d. by 42 cm gold-coated Pyrex light pipe (246°C) using a 0.25 mm i.d. gold-coated nickel transfer line (250°).[11]

Interferograms (later transformed to infrared spectra) of the GC effluent in the light pipe were acquired using the following parameters: 32 scans background; 4 scans coadded for each data file; 2048 data points/spectrum; 4096 transform points/spectrum (8 cm^{-1} nominal resolution); scan velocity set at 34 (0.533 cm/s or about 0.82 s/scan); and Happ-Genzel apodization.

The GC effluent was monitored in real time by construction of a "chemigram." Infrared bands were selected to monitor specific chemical group frequencies. The four scans constituting each data file were coadded, transformed at low resolution (32 cm^{-1}), and integrated over the bands, and the intensity was plotted. If the intensity in any band exceeded the threshold set at an absorbance

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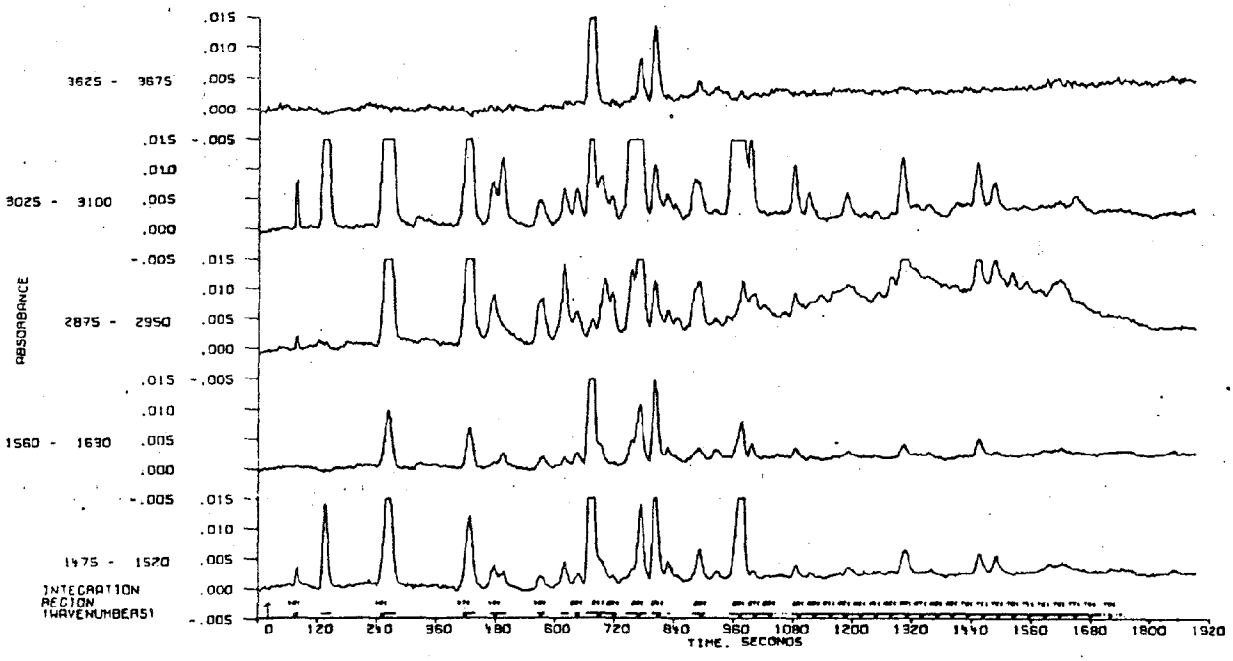

FIG. 1. Chemigram of infrared bands (wavenumbers) vs time during GC/FT-IR analysis of extract of XAD-2 sorbent sampled during surge phase of a coal gasification run.

of 0.005, the data file was stored (as the interferogram) on the magnetic disk for subsequent manipulation.

II. RESULTS AND DISCUSSION

A chemigram of the sample is shown in Fig. 1. The band from 3625 to 3675 cm^{-1} is selective for the hydroxyl group, the 3025 to 3100 cm^{-1} band is selective for unsaturated hydrocarbons (e.g., aromatics), the 2875 to 2950 cm^{-1} is selective for alkanes, the 1560 to 1630 cm^{-1} band is indicative of aromatics, and the 1475 to 1520 cm^{-1} band is characteristic of aromatics (C=C stretch) and alkanes (C—H bend). Inspection of the chemigram alone indicates that 20 to 30 peaks may be attributed to aromatics, many of them alkyl aromatics. Three large peaks and one small peak in the 3625 to 3675 cm^{-1} band indicate the presence of phenolic compounds. For many purposes, the information obtainable from the chemigram may be sufficient. Appropriate choices of chemigram bands can quickly indicate the presence or absence of certain functional groups as illustrated by the 3625 to 3675 cm^{-1} band. Another analysis of this sample using a 1700 to 1730 cm^{-1} window indicated that carbonyl-containing compounds were not present to any significant extent.

Interpretation of the chemigram indicated that most (but not all) of the compounds in this sample were alkyl aromatics. In addition, a few phenolic compounds were observed. Aliphatic compounds do not appear to be present in significant concentrations. For the purpose of screening samples for selected functional groups, the chemigram may be sufficient. Interpretation of this data is quick, requires no further manipulation of data, and does not require standard spectra for comparison.

Spectra were stored on the magnetic disk at every file position indicated by a tic-mark along the x-axis of the chemigram. The full spectra were transformed, ratioed against background, and plotted for selected files of interest. The spectra were interpreted by comparison with authentic gas phase spectra generated in our laboratory

TABLE I. Compounds identified in XAD-2 surge sample from coal gasification run shown in Fig. 1.

Retention time (s)	File no.[a]	Compound[b]
69	451	Methylene chloride (solvent)
126	455	Benzene
264	465	Toluene
422	474	*m*-Xylene (tentative)
475	480	*o*-Xylene (tentative)
491	486	Ethyl benzene (tentative)
564	490	1,3,5-Trimethylbenzene (tentative)
608	495	1,2,4-Trimethylbenzene (tentative)
642	502	Alkyl benzene
671	507	Phenol
697	515	Monosubstituted alkyl benzene (tentative)
720	521	Indan (tentative)
760	526	Indene
776	532	*o*-Cresol and *p*-cresol (?)
800	539	*m*-Cresol
830	544	Alkyl benzene
890	548	2,6-Xylenol
905	553	2,4-Xylenol
967	560	Naphthalene
998	568	1-Methylnaphthalene (tentative)
1080	589	2-Methylnaphthalene (tentative)
1110	594	Alkyl aromatic
1170	617	Alkyl aromatic
1308	661	Ester (background)
1445	708	Dimethylnaphthalene isomer (tentative)
1483	720	1,4-Dimethylnaphthalene (tentative)

[a] File positions are located along the x-axis of Fig. 1.
[b] Identifications made by comparison with standard gas phase spectra. Where gas phase spectra were unavailable, tentative identifications were made using standard condensed-phase spectra.

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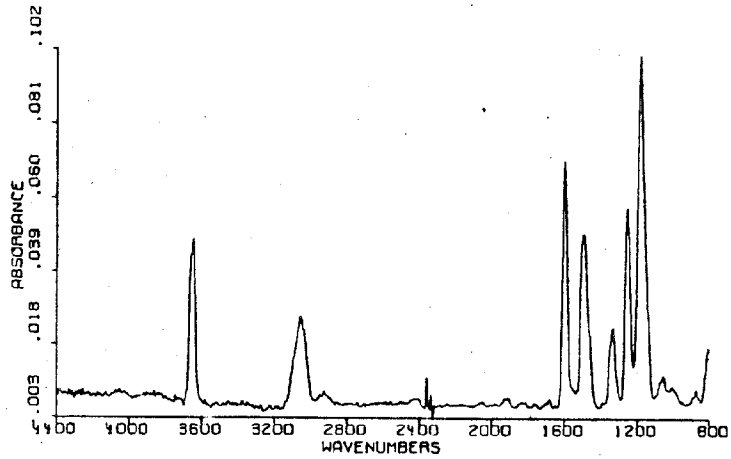

FIG. 2. Gas phase infrared spectrum of file no. 507 in Fig. 1; identified as phenol.

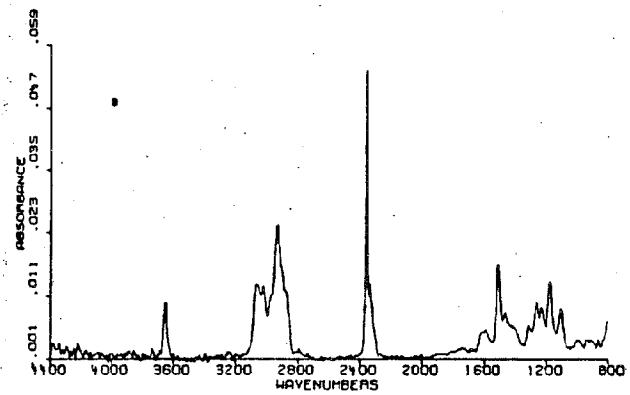

FIG. 3. Gas phase infrared spectra of file no. 553 in Fig. 1; identified as 2,4-xylenol.

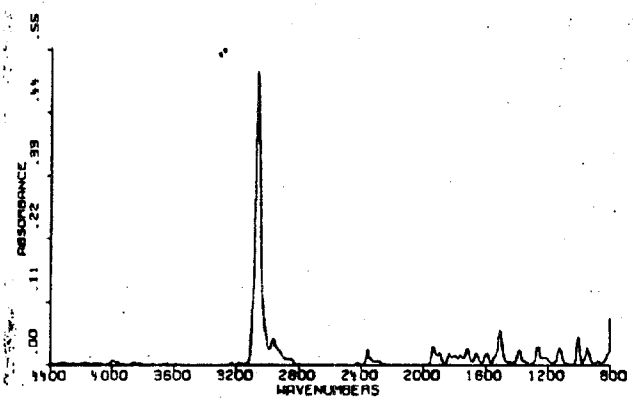

FIG. 4. Gas phase infrared spectrum of file no. 560 in Fig. 1; identified as naphthalene.

using standards or with spectra from the literature.[12] Where standard gas phase spectra were unavailable, spectra were tentatively identified by comparison with condensed phase spectra.[13] The compounds identified are presented in Table I. Examples of the infrared spectra are presented in Figs. 2 to 4. The specificity of the compound identifications in Table I illustrates the power of GC/FT-IR. Routine interpretation of gas chromatography-mass spectrometry data would not have specified the positional isomers for many of the alkyl aromatics and alkyl phenols. The ability to distinguish isomers is important for environmental assessment of coal gasification due to the difference in toxicity, carcinogenicity, and mutagenicity of isomeric compounds.

These results demonstrate the feasibility of using GC/FT-IR for analysis of semivolatile organics in coal gasification effluents. The utility of both the chemigram for quick class identification and the individual spectra for identification of individual components is a major asset of the technique.

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